NON-CERTIFIED, UNFORMATTED TRANSLATION FROM INTERLINGUA.COM

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(54) Title of the invention
Spin Processor

(57) Abstract
Objective:
To offer a cleaning apparatus that adequately manifests the respective merits of liquid phase cleaning and gas phase cleaning.

Constitution:
A spin processor **10** is equipped with a rotating rotor **2** in a cleaning chamber **1**. A cleaning liquid supply pipe **16** that sprays cleaning liquid protrudes into the rotor **2**, and a cleaning gas supply pipe **18** is connected to the cleaning chamber **1**. During cleaning, a carrier **9** on which Si wafers **W** have been placed is placed in the rotor **2**, and as it is rotated by the motor **3**, cleaning liquid is sprayed so that liquid phase cleaning is carried out. After liquid phase cleaning, HF vapor is then introduced from the cleaning gas supply pipe **18** and is conducted into the carrier **9** via the holes **11** in the rotor **2** so that oxide film produced due to liquid phase cleaning is cleaned by the gas phase. No drying is performed after removal of the oxide film, so that the number of processes is reduced relative to conventional cleaning treatments. A cleaning treatment can thus be carried out that provides the merits of both.

Claims
Claim 1. A spin processor, characterized by being equipped with a cleaning chamber, a rotor that contains the object to be cleaned and can rotate within the aforementioned cleaning chamber, a cleaning liquid supply pipe that is connected to the cleaning chamber and supplies liquid cleaning agent to the

interior of the aforementioned rotor that rotates, and a cleaning gas supply pipe that is connected to the cleaning chamber and supplies gas cleaning agent to the interior of the rotor.

Claim 2. The spin processor according to Claim 1, characterized in that the aforementioned cleaning liquid supply pipe is equipped with a tip section that protrudes into the center of the rotor, numerous spray openings that discharge cleaning liquid into the rotor interior in the form of a mist are formed at the aforementioned tip section, and numerous holes are formed in the side walls of the rotor, which conduct cleaning gas that has been introduced into the cleaning chamber into the rotor interior.

Claim 3. The spin processor according to Claim 2, characterized in that exhaust pipes that conduct cleaning liquid and cleaning gas from the chamber after cleaning are connected to the aforementioned cleaning chamber.

Detailed description of the invention

[0001]

Field of industrial utilization

The present invention concerns a cleaning device for cleaning Si wafers or other objects to be cleaned, and in particular, concerns a spin processor that is designed so that the cleaning treatment can be effectively performed by housing and rotating the object to be cleaned.

[0002]

Prior art

In recent years, the detail of circuit patterns has been increasing in the field of semiconductor electronics, and the degree of large-scale integration is trending towards higher densities and higher integration levels. In conjunction therewith, micro-contamination present on wafers has come to have a significant effect on product quality and productivity. For this reason, the cleanliness of various processes such as ultra-large scale integrated circuit manufacture processes must, of course, be increased, and the degree to which the surface of the wafer is maintained in a clean state has become a critical problem. Consequently, the wafer cleaning processes are becoming extremely important processes.

[0003]

At present, cleaning of wafers is carried out by liquid-phase cleaning methods (wet cleaning) wherein SC1 cleaning liquid (ammonia and hydrogen peroxide aqueous solution) or SC2 cleaning liquid (hydrochloric acid and hydrogen peroxide aqueous solution) are used as cleaning agents, and gas-phase cleaning methods (dry cleaning) wherein a gas such as HF vapor or UV/O_3 is used. At present, liquid-phase cleaning treatments are primarily used for various reasons, for example, because throughput (treatment volume per unit time) is high due to the potential for batch treatments, cleaning of the back side of the wafer is also possible, and numerous types of contaminants such as particles and natural oxide films can be eliminated with comparative ease. However, this type of wafer cleaning method brings with it the problem that contaminants accumulate in the cleaning agent when the liquid cleaning agent is used over a long period of time, and re-contaminate wafers by adhering to the surface of wafers arriving from previous processes. Although it is desirable, in theory, to always use fresh cleaning liquid or purified water, cleaning liquid consumption increases in such cases, which causes an increase in manufacture cost.

[0004]

By means of [illegible due to missing line at bottom], cleaning can be carried out uniformly at the micro-region level, e.g., contact holes, and moreover, the aforementioned type of re-contamination will not occur, leading to the advantage that the device can be readily used in combination with equipment such as cluster tools. With this type of dry cleaning method, however, there are problems with particle removal, which is a critical cleaning objective.

[0005]

Consequently, there are manufacture processes wherein two cleaning treatment processes, wet cleaning and dry cleaning, are combined in the wafer manufacture process. By this means, the attempt is made to increase cleanliness to as high a level as possible by combining the merits of each method.

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[0006]
Problems to be solved by the invention
However, with this type of cleaning method, there is a strong possibility that new contaminating material will adhere to the surface of the wafer in the process whereby the wafer is transported from wet cleaning to dry cleaning. In addition, transport of the object to be cleaned in itself requires work during the cleaning treatment process, and productivity is greatly increased. Moreover, two cleaning apparatuses cannot readily be incorporated in cluster tools.
[0007]
The present invention has the objective of offering a cleaning device that makes adequate use of the merits of both liquid phase cleaning and gas phase cleaning, without causing problems of this type.
[0008]
Means for solving the problems
In order to attain the aforementioned objectives, the spin processor of the present invention is characterized by being equipped with a cleaning chamber, a rotor that contains the object to be cleaned and can rotate within the aforementioned cleaning chamber, a cleaning liquid supply pipe that is connected to the cleaning chamber and supplies liquid cleaning agent to the interior of the aforementioned rotor that rotates, and a cleaning gas supply pipe that is connected to the cleaning chamber and supplies gas cleaning agent to the interior of the rotor.
[0009]
In addition, the cleaning liquid supply pipe of the spin processor is equipped with a tip section that protrudes into the center of the rotor, where numerous spray holes that discharge cleaning liquid into the rotor interior in the form of a mist are formed on the aforementioned tip region. Moreover, numerous holes that conduct cleaning gas that has been introduced into the cleaning chamber into the rotor interior are formed in the side walls of the rotor.
[0010]
Action
A cleaning liquid supply pipe that supplies liquid cleaning agent and a cleaning gas supply pipe that supplies gas cleaning agent are connected to the cleaning chamber, and because these agents can be supplied to the rotor interior, both liquid phase cleaning and gas phase cleaning are possible within a single cleaning chamber, so that cleaning can be carried out while manifesting the merits of both methods. In addition, it is possible to rotate the rotor in the cleaning chamber, so that the tip section of the cleaning liquid supply pipe that protrudes into the center thereof causes the cleaning liquid to completely cover the interior of the rotor, thereby ensuring uniform cleaning.
[0011]
Working example
The spin processor of the present invention was [illegible due to missing line at bottom], and as an application example of the present invention a device is shown exhibiting a batch-format spin processor structure wherein Si wafers that are in an orderly arrangement in a carrier are subjected to liquid phase and gas phase cleaning in this condition. In the figure, **10** denotes the spin processor body, and **W** denotes each of the Si wafers that are the objects to be cleaned.
[0012]
The spin processor **10** is equipped with a cylindrical cleaning chamber **1**, with a cylindrical rotor **2** that is slightly smaller than the cleaning chamber **1** being installed on the interior of the cleaning chamber. The rotor **2** is formed so that it can be driven to rotate in the cleaning chamber by a motor **3** that is installed in the floor of the cleaning chamber, with the drive axle **4** of the motor **3** passing through the bottom wall **5** of the cleaning chamber, and attaching at the center of the rotor base plate **6**.
[0013]
The rotor **2** is a cylinder that is assembled from a circular rotor base plate **6**, an annular side plate **7** and a rotor ceiling plate **8** that is carried on the side plate. The rotor ceiling plate **8** can be attached or removed freely on the rotor body so that it is possible to introduce or remove the carrier **9** described below. In

addition, numerous passage holes **11** are formed over the entire region of the side plate **7** passing between the interior and exterior of the rotor.

[0014]
During operation of the spin processor, a common square carrier **9** that carriers numerous Si wafers **W** is housed in the interior space of the rotor. The carrier **9** is assembled from a mesh plate, for example, so that it allows flow of cleaning liquid via the carrier walls, and as shown in the figure, multiple cells **12** are formed that each house a single sheet of wafer **W**, so that each of the Si wafers **W** do not contact other wafers **W** in the carrier.

[0015]
In the spin processor **10** constituted in the manner described above according to this working example, a bushing **14** that fits into the rotor ceiling plate **8** so that it can rotate is fixed to the inside of the center of the cleaning chamber ceiling plate **13**. A passage hole **15** is also formed in the bushing **14** and in the cleaning chamber ceiling plate **13**, thus passing between the cleaning chamber exterior and rotor interior. The pipe **16** for supplying cleaning liquid is inserted and fixed therein, and cleaning liquid is supplied as indicated by the arrow **B**. The tip section of the cleaning supply pipe **16** descends from the bushing **14** inside the carrier **9**, and cleaning liquid is sprayed onto the Si wavers **W** in the carrier from the numerous spray openings **17** that are formed in the pipe periphery. This device is thus referred to as a wet cleaning device.

[0016]
In addition, in this working example, a cleaning gas supply pipe **18** that supplies cleaning gas (for example HF vapor) as indicated by the arrow **A** to the cleaning chamber interior from a gas supply source not shown in the figure is connected to the cleaning chamber roof plate **13**. This cleaning gas supply pipe **18**, as shown in the figure, is intentionally connected at the periphery of the cleaning chamber ceiling plate **13** in such a manner that the cleaning gas that is conducted into the cleaning chamber proceeds smoothly to the interior of the rotor via the aforementioned holes **11** . With respect to this cleaning chamber 1, the aforementioned various supply [illegible due to missing line at bottom] and an exhaust pipe **19** for exhausting [illegible due to missing line at bottom] liquid, cleaning gas) outside the cleaning chamber as indicated by the arrow **C** and a waste water pipe **20** for removing cleaning liquid as shown by the arrow **D** are each connected in the lower part of the cleaning chamber.

[0017]
Next, the action of the aforementioned spin processor **10** and an example of a cleaning method using this device will be discussed using, as an example, common RCA cleaning comprising SC1 cleaning (ammonia and hydrogen peroxide aqueous solution) and SC2 cleaning (hydrochloric acid and hydrogen peroxide aqueous solution).

[0018]
Figure 2a shows the wafer cleaning sequence carried out using the spin processor **10**. Prior to cleaning, the cleaning chamber ceiling plate **13** and the rotor ceiling plate **8** first are removed from the cleaning chamber and the carrier body respectively, and then the carrier **9** with the Si wafers **W** inserted therein is placed in the rotor using an appropriate transport means so that each of the wafers is horizontal. After placing, the cleaning chamber ceiling plate **13** and the rotor ceiling plate **8** are installed on the cleaning chamber body and carrier body respectively. Next, SC1 is discharged in the form of a spray inside the rotor from the cleaning liquid supply pipe **16** at the center of the cleaning chamber, and simultaneously, the rotor **2** is made to rotate by means of the motor **3**, thereby spin-cleaning the Si wafers **W**. Subsequently, the cleaning liquid is supplied to the interior of the rotor via the cleaning liquid supply pipe **16** in the sequence: SC1 //arrow// DIW (purified water cleaning used in order to control change in hydrogen ion concentration due to SC1) //arrow// SC2 //arrow// DIW. Liquid phase cleaning of the wafers is thus carried out in this manner.

[0019]
Upon completion of liquid phase cleaning, rotation of the rotor **2** is halted after a determinate period of time, and the wafers **W** are dried. Subsequently, the wafers are transitioned to gas phase cleaning using

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HF vapor. The HF vapor is supplied between the cleaning chamber 1 and rotor 2 via a cleaning gas supply pipe **18**, and is conducted to the rotor interior via holes **11** that have been provided in the rotor side wall 7. In order to improve the cleaning uniformity and diffusion of vapor at this time, the rotor **2** is rotated. By means of gas phase cleaning using HF vapor, the natural oxide films that have formed on the wafer due to liquid phase cleaning are removed. After gas phase cleaning, the carrier **9** is removed from the cleaning chamber 1 unchanged, and is transported to subsequent processes (a drying process is unnecessary due to gas phase cleaning).

[0020]

When the spin processor 10 of the present invention is used in this manner, both liquid phase cleaning and gas phase cleaning can be carried out almost simultaneously in a single vessel, so that the particles present on the Si wafers **W** can be removed by gas phase cleaning and recontamination can be controlled by gas phase cleaning.

[0021]

Moreover, gas phase cleaning carried out using HF vapor does not require a drying process after cleaning, as is well known, and thus includes the drying treatment after DHF (fluoric acid aqueous solution cleaning treatment) as shown in Figure 2b. As a result, the treatment time is short relative to conventional liquid phase cleaning methods, and productivity can be improved. Of course, in comparison to conventional methods in which liquid phase cleaning and gas phase cleaning are carried out using separate equipment, because transport is not performed between cleaning operations, contamination during this period [illegible due to missing line].

[0022]

In addition, with this spin processor **10**, numerous wafers placed in the carrier **9** are cleaned at the same time, giving high throughput because a "batch-format" cleaning method can be employed, and moreover, cleaning of the back surface of the wafer can be carried out simultaneously.

[0023]

Another method for using the spin processor **10** involves introducing gas of the cleaning liquid component into the cleaning chamber interior through the cleaning gas supply pipe **18**, while introducing purified water into the rotor via the cleaning liquid supply pipe **16**, thus allowing absorption of the gas into the purified water so that clean cleaning liquid can be produced in the rotor. This cleaning liquid is immediately used for cleaning the wafers, and thus liquid phase cleaning can be carried out using cleaning liquid that is unaffected by the purity of the reagents.

(0024)

Moreover, although a batch-format spin processor was used in this working example, the aforementioned structure can also be used in a sheet-format spin processor.

[0025]

Effect of the invention

As described above, liquid phase cleaning and gas phase cleaning can be carried out in the present invention in a single cleaning chamber, and thus the cleaning process can be carried out while manifesting the merits of each.

[0026]

The cleaning process can be shortened relative to conventional methods, and adhesion of contaminants during transport can be prevented because no transport occurs between cleaning processes.

Brief description of the figures

Figure 1. Cross-sectional diagram of the spin processor of a working example of the present invention.

Figure 2. Diagram showing (a) the cleaning process sequence using the spin processor of the present invention, and (b) the cleaning process sequence of a conventional method.

Key:

1 Cleaning chamber

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2 Rotor
3 Carrier
10 Spin processor
16 Cleaning liquid supply pipe
18 Cleaning gas supply pipe
W Si wafer

Figure 1
//insert//

Figure 2
//insert//
(a)
1 Liquid phase cleaning
2 Gas phase cleaning

(b)
1 Liquid phase cleaning

-2- (WPAT)

AN - 96-102548/11

XRPX- N96-085961

TI - Washing device with spin processor for e.g. silicon wafer - has washing gas supply pipe which supplies washing gas to inside of rotor and washing liquid supply pipe which supplies liquid washing agent to inside of rotor

DC - P43 U11

AW - SPIN PROCESSOR

PA - (SONY) SONY CORP

PR - 94.06.22 94JP-164469

NUM - 1 patent(s) 1 country(s)

PN -- JP08008222 A 96.01.12 * (9611) 4p H01L-021/304

AP -- 94JP-164469 94.06.22

IC1 - H01L-021/304

IC2 - B08B-003/02 B08B-007/04

AB - JP08008222 A

The washing device comprises a rotor (2) which rotates inside a washing chamber (1) and a washing liquid supply pipe (16) which is projected into the rotor for supplying washing liquid. A carrier (9) is provided in a rotor and an Si wafer (W) is set up inside the carrier. The supplied washing liquid is ~~rotated by a motor (3).~~

A washing gas supply pipe (18) is provided which supplies washing gas agent after finishing liquid phase washing. A number of holes (11) are provided to the rotor which enable the gas to enter into the carrier. An oxide film which adheres by liquid phase washing is removed by gaseous phase washing.

USE/ADVANTAGE - For VLSI mfg. process. Prevents dryness after oxide film removal. Reduces number of process. Employs each merit efficiently. Performs gaseous phase washing and liquid phase washing in same chamber. (Dwg.1/2)

FN - WPG274K1.GIF

1020 SC1 = N[redacted]H / SC2 = HCl
H_2O_2 H_2O_2
H_2O

wash Si in liquid + form SiO_2 → HF vapor etch SiO_2 } rotate wafer

prodrying step

Kajita et. al

-9- (JAPIO)

AN - 96-008222

TI - SPIN PROCESSOR

PA - (2000218) SONY CORP

IN - KAJITA, CHIHO

PN - 96.01.12 J08008222, JP 08-8222

AP - 94.06.22 94JP-164469, 06-164469

SO - 96.01.12 SECT. , SECTION NO. ; VOL. 96, NO. 1.

IC - H01L-021/304; B08B-003/02; B08B-007/04

JC - 42.2 (ELECTRONICS--Solid State Components); 28.1 (SANITATION--Sanitary Equipment)

NE

AB - PURPOSE: To provide a cleaning apparatus, which can sufficiently utilize the respective merits of liquid phase cleaning and gaseous phase cleaning.

CONSTITUTION: A spin processor 10 has a rotor 2, which is rotated in a cleaning chamber 1. A cleaning-liquid supplying pipe 16 for spraying cleaning liquid protrudes into the inside of the rotor 2. A changing-gas supplying pipe 18 is connected to the cleaning chamber 1. At the time of the cleaning, a carrier 9, wherein Si wafers W are set, is placed in the rotor 2 and rotated by a motor 3, and the cleaning liquid is injected. Thus, the liquid-phase cleaning is performed. After the liquid-phase cleaning, HF vapor is introduced through the cleaning-gas supplying pipe 18 and introduced into the carrier 9 through holes 11 of the rotor 2, and an oxide film formed by the liquid phase cleaning undergoes the gas-phase cleaning. Since there is no drying after the removal of the oxide film, the number of steps becomes less than of the conventional cleaning process, and the cleaning process, which utilizes both merits, can be performed.

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			N			
B08B	3/02		Z	2119-3B		
	7/04		Z			

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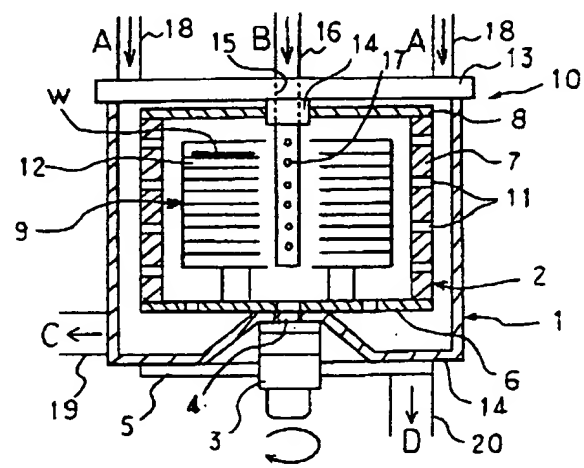
103-(1-3, 10-11, 14-18　24-25)

(54)【発明の名称】　スピンプロセッサ

(57)【要約】
【目的】　液相洗浄および気相洗浄それぞれのメリットを充分生かせる洗浄装置を提供する。
【構成】　スピンプロセッサ１０は、洗浄チャンバ１内で回転するロータ２を備える。ロータ２の内部には洗浄液をスプレィする洗浄液供給管１６が突き出し、洗浄チャンバ１には洗浄ガス供給管１８が接続される。洗浄時、ＳｉウェーハＷをセットしたキャリア９がロータ２内部に置かれ、モータ３によって回転されながら洗浄液が噴射され、液相洗浄がおこなわれる。液相洗浄後、こんどは洗浄ガス供給管１８よりＨＦベーパーが導入され、ロータ２の穴１１を介してキャリア９内に導かれ、液相洗浄によって付着した酸化膜が気相洗浄される。酸化膜除去後は乾燥がないために従来の洗浄処理よりも工程数が少なくなり、双方のメリットを生かした洗浄処理が可能となる。



【特許請求の範囲】

【請求項1】　洗浄チャンバと、被洗浄物を収納して前記洗浄チャンバ内で回転可能なロータと、洗浄チャンバに接続され、回転する前記ロータの内部に液体洗浄剤を供給する洗浄液供給管と、洗浄チャンバに接続され、ロータ内部に気体洗浄剤を供給する洗浄ガス供給管とを備えたことを特徴とするスピンプロセッサ。

【請求項2】　前記洗浄液供給管は、ロータの中央に突出する先端部分を備え、前記先端部分には洗浄液を霧状にしてロータ内部に噴出させる多数の噴口が形成され、ロータの側板には洗浄チャンバ内に導入された洗浄ガスをロータ内部に導く多数の穴が形成されることを特徴とする請求項1に記載のスピンプロセッサ。

【請求項3】　前記洗浄チャンバには、洗浄後の洗浄液および洗浄ガスをチャンバ外に導く排出管が接続されることを特徴とする請求項2に記載のスピンプロセッサ。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、例えばＳｉウェーハなどの被洗浄物を洗浄する洗浄装置に関し、特に被洗浄物を収納して回転させることにより効果的に洗浄処理が行われるようにしたスピンプロセッサに関する。

【0002】

【従来の技術】近年、例えば半導体エレクトロニクスの分野などでは、回路パターンの微細化が進み、ＬＳＩが一層高密度、高集積化する傾向にあり、これに伴ってウェーハ上へのマイクロコンタミーネション（微小汚染）が、製品品質や生産性に大きな影響を及ぼすようになってきた。このため、超ＬＳＩ製造工程などでは各工程を清浄化することは勿論のこと、ウェーハ表面をいかに清浄に保つかが重要な課題となってきており、この点でもウェーハの洗浄工程は極めて重要な工程となっている。

【0003】現在、ウェーハの清浄には、洗浄材としてＳＣ１洗浄液（アンモニア過酸化水素水）やＳＣ２洗浄液（塩酸過酸化水素水）などの液体を使用する液相洗浄（ウェット洗浄）と、ＨＦベーパーやＵＶ／O_3などの気体を使用する気相洗浄（ドライ洗浄）があり、現時点では液相洗浄処理が主流となっている。これは、ウェット洗浄が、バッチ処理が可能でありスループット（単位時間当たりの処理量）が大きいことや、またウェーハの裏面洗浄も可能であること、また更にパーティクル、自然酸化膜など複数の汚染物を比較的簡単に除去可能であること、などの諸々の理由によるものである。しかしながら、このウェーハ洗浄法においては、液体洗浄剤の長期使用に伴って、洗浄剤中に蓄積された汚染物質が前工程からくるウェーハの表面に付着する再汚染という問題を抱えている。従って、理想的には常に新しい洗浄液や純水を使用すればよいが、この場合洗浄液の消費量が増加し、製造コストの上昇を招くことになる。

によりコンタクトホールなどの微細部まで均一に洗浄できることに加え、上述したような再汚染が少なく、またクラスターツールなどの設備に容易に組み込むことができる利点がある。しかしながら、このドライ洗浄では洗浄の主目的であるところのパーティクル除去が困難である。

【0005】従って、現在ではウェーハ製造工程にウェット洗浄とドライ洗浄の２つの洗浄処理工程を組み入れ、双方のそれぞれのメリットを生かすようにしてウェーハを出来るだけ高いレベルで清浄化しようとした製造工程もある。

【0006】

【発明が解決しようとする課題】しかしながら、このような洗浄方法においては、例えばウェット洗浄からドライ洗浄に至るまでの搬送過程で、新たに汚染物質がウェーハ表面に付着する可能性が高い。また、この方法では洗浄処理工程間の被洗浄物の搬送自体に手間が要し、生産性が著しく低下するばかりか、簡単にクラスターツール内に２つの洗浄設備を組み込めるというものでもない。

【0007】本発明は、このような問題を生じることなく、液相洗浄および気相洗浄それぞれのメリットを充分生かせる洗浄装置を提供することを目的とする。

【0008】

【課題を解決するための手段】上記目的を達成するため、本発明によるスピンプロセッサは、洗浄チャンバと、被洗浄物を収納して前記洗浄チャンバ内で回転可能なロータと、洗浄チャンバに接続され、回転する前記ロータの内部に液体洗浄剤を供給する洗浄液供給管と、洗浄チャンバに接続され、ロータ内部に気体洗浄剤を供給する洗浄ガス供給管とを備えたことを特徴としている。

【0009】また、好ましくは、このスピンプロセッサの洗浄液供給管は、ロータの中央に突出する先端部分を備え、前記先端部分には洗浄液を霧状にしてロータ内部に噴出させる多数の噴口が形成され、更にロータの側板には洗浄チャンバ内に導入された洗浄ガスをロータ内部に導く多数の穴が形成される。

【0010】

【作用】洗浄チャンバに、液体洗浄剤を供給する洗浄液供給管と気体洗浄剤を供給する洗浄ガス供給管を接続し、ロータ内部に供給可能とすることで、１つの洗浄チャンバ内で液相洗浄と気相洗浄の双方が可能となり、双方のメリットを生かした洗浄を行うことができる。また、ロータを洗浄チャンバ内で回転可能とし、中央に洗浄液供給管の先端部分を突出させたことで、洗浄液がくまなくロータ内部に行き渡り、洗浄ムラを無くすことができる。

【0011】

【実施例】図面を参照しながら本発明によるスピンプロ

は、本発明の一実施例として、キャリア内に順序よく配置されたＳｉウェーハを、そのままの状態で液相および気相洗浄するバッチ式のスピンプロセッサの構造を示したものである。本図において、１０はスピンプロセッサ本体、Wは被洗浄物としてのＳｉウェーハをそれぞれ示している。

【００１２】スピンプロセッサ１０は円筒形の洗浄チャンバ1を備えており、洗浄チャンバ内部には洗浄チャンバ1よりも一回り小さな円筒形のロータ２が設けられる。ロータ２は洗浄チャンバ底部に設置されたモータ３によって洗浄チャンバ内部で回転駆動されるようになており、このためにモータ３の駆動軸４は洗浄チャンバ底壁５を貫通してロータ底板６の中央に固着されている。

【００１３】ロータ2は、円形のロータ底板６と環状の側板７、およびこの側板上に載るロータ天板８から組み立てられる円筒体であって、ロータ天板８は後述するキャリア９の出し入れを可能とするべくロータ本体に対して着脱自在となっている。また、側板７にはロータ内部と外部とを連通する穴１１が全域に亙って多数形成される。

【００１４】スピンプロセッサ作動時、このロータ内部空間には、多数のＳｉウェーハWを保持する通常の四角状キャリア９が収納される。キャリア９は、キャリア壁を介した洗浄材の流動を可能にするため、例えばメッシュ板によって組み立てられ、図示するように、キャリア内においては、それぞれのＳｉウェーハWが他のウェーハWと接することがないように1枚のウェーハWを収容する多数セル１２が形成されている。

【００１５】以上のように構成されるスピンプロセッサ１０において、本実施例によれば、洗浄チャンバ天板１３の中央部の内側にはロータ天板８に回転可能に嵌合するブッシュ１４が固定される。ブッシュ１４および洗浄チャンバ天板１３には洗浄チャンバ外部とロータ内部とを連通する貫通孔１５が形成され、ここに、洗浄液供給管１６が差し込み固定され、洗浄液が矢印Ｂのように供給される。洗浄供給管１６の先端部分はブッシュ１４よりキャリア９の内部へと垂下し、管周囲に形成された多数の噴口１７より、キャリア内のＳｉウェーハWに対し洗浄液を吹き付け、いわゆるウェット洗浄するものである。

【００１６】更に、本実施例によれば、洗浄チャンバ天板１３には、図示しないガス供給源から洗浄チャンバ内部に対して洗浄ガス（例えば、ＨＦベーパー）を矢印Ａのように供給する洗浄ガス供給管１８が接続される。この洗浄ガス供給管１８は、図示するように洗浄チャンバ天板１３の周縁近傍部分に接続され、洗浄チャンバ内に送り込まれた洗浄ガスが、前出の穴１１を介してロータ内部にスムーズに進入するような配慮がなされている。なお、この洗浄チャンバ1に対しては、上述した各供給

液、洗浄ガス）を洗浄チャンバ外部へと矢印Ｃのように排出するための排気管１９および洗浄液を矢印Ｄのように排出する排水管２０が、洗浄チャンバ下部にそれぞれ接続される。

【００１７】次に、ＳＣ１（アンモニア過酸化水素水洗浄）とＳＣ２（塩酸過酸化水素水洗浄）からなる一般的なＲＣＡ洗浄を例にとり、上述したスピンプロセッサ１０の作動およびこれを用いた洗浄方法例を説明する。

【００１８】図２（ａ）はスピンプロセッサ１０を使用するウェーハ洗浄手順を示している。洗浄に先立って、まず洗浄チャンバ天板１３およびロータ天板８を洗浄チャンバ本体、キャリア本体からそれぞれ取り外し、次にＳｉウェーハWを入れたキャリア９を、適当な搬送手段を用いてロータ内部に、各ウェーハWが水平になるようにセットする。セット後は再び洗浄チャンバ天板１３、ロータ天板８をそれぞれ洗浄チャンバ本体、キャリア本体に取り付ける。次に、洗浄チャンバ中心の洗浄液供管１６からロータ内部にＳＣ１をスプレィ状態で噴射し、同時にモータ３によりロータ２を回転させて、ＳｉウェーハWをスピン洗浄する。その後、洗浄液はＳＣ１→ＤＩＷ（ＳＣ１によるペーハー変化を調整するための純水洗浄）→ＳＣ２→ＤＩＷというように順次洗浄液供給管１６を介してロータ内部に供給され、このようにしてウェーハの液相洗浄が行われる。

【００１９】液相洗浄が終了したならば、次に所定時間に亙ってロータ２を回転継続しウェーハWを乾燥させ、次にＨＦベーパーによる気相洗浄へと移行する。ＨＦベーパーは洗浄ガス供給管１８を介して、まず洗浄チャンバ1とロータ２の間の空間に供給され、ロータ側板７に設けられた穴１１を通ってロータ内部へと導入される。なお、この時ベーパーの拡散性と洗浄均一性を向上させるため、ロータ２は回転される。このＨＦベーパーを用いた気相洗浄により、液相洗浄によってウェーハ表面に形成された自然酸化膜は除去される。そして気相洗浄後、キャリア９はそのまま洗浄チャンバ1より取り出され、後工程へと搬送されるのである（気相洗浄のため、乾燥処理は不要）。

【００２０】このように、本発明のスピンプロセッサ１０を使用すると、１つの容器内で液相洗浄と気相洗浄の双方をほぼ同時に行うことができ、液相洗浄でＳｉウェーハW上のパーティクルを除去し、かつ気相洗浄でコンタミネーションの再付着を抑制することができる。

【００２１】また、ＨＦベーパーによる気相洗浄は、当然ながら洗浄後の乾燥処理を必要としないため、図２（ｂ）に示したようなＤＨＦ（フッ酸溶液洗浄処理）後の乾燥処理を含む、従来の液相洗浄方法に比較して処理時間が短く、生産性を高めることができる。当然、液相洗浄と気相洗浄を別の設備で行う従来方法との比較においても、洗浄工程間の搬送がないために、この間の汚染

【００２２】更に、このスピンプロセッサ１０は、キャリア９に多数のウェーハをセットして一括して洗浄する、所謂バッチ式洗浄法を採用しているためスループットが高く、またウェーハ裏面の洗浄も同時に行うことができる。

【００２３】なお、このスピンプロセッサ１０の別の活用法としては、洗浄ガス供給管１８を介して洗浄チャンバ内部に洗浄液成分のガスを導入し、洗浄液供給管１６を介してロータ内部に純水を導入すると、この純水にガスが吸収され、クリーンな洗浄液をロータ内で作製することができる。この洗浄液を直ちにウェーハ洗浄に使用した場合、薬品の純度に依存しない洗浄液による液相洗浄が可能となる。

【００２４】また、実施例ではバッチ式のスピンプロセッサとしたが、当然、枚葉式のスピンプロセッサにも上述した構造は適用可能である。

【００２５】

【発明の効果】以上説明したように、本発明によれば、１つの洗浄チャンバ内で液相洗浄と気相洗浄が行うことが可能となり、それぞれのメリットを生かした洗浄処理が可能となる。

【００２６】また、従来と比較して洗浄工程も短縮でき、洗浄工程間の搬送もなく汚染物質の搬送時付着を防止することができる。

【図面の簡単な説明】

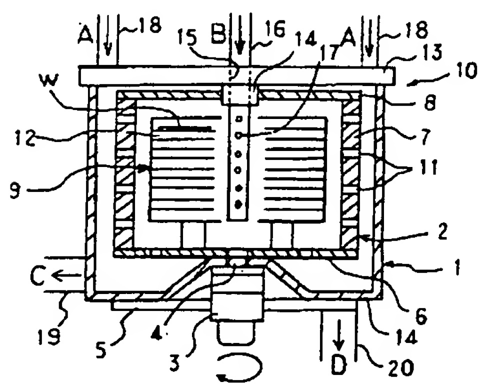
【図１】　本発明の一実施例によるスピンプロセッサの断面図である。

【図２】　洗浄工程の流れを示し、（ａ）は本発明のスピンプロセッサを使用した洗浄工程の流れ、（ｂ）は従来の洗浄工程流れを示した図である。

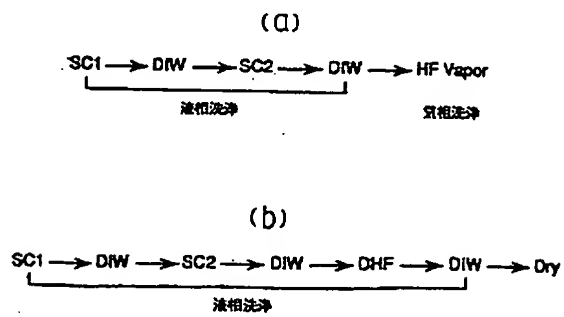
【符号の説明】

１…洗浄チャンバ
２…ロータ
９…キャリア
１０…スピンプロセッサ
１６…洗浄液供給管
１８…洗浄ガス供給管
W…Ｓｉウェーハ

【図１】



【図２】



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Specifications

1. Name of Invention

Cleaning Method for Silicon Wafer

2. Claims

(1) A method for cleaning a silicon wafer is characterized by a cleaning liquid comprised of an aqueous solution that contains 0.1 – 20 wt% hydrogen fluoride during the silicon wafer cleaning process, along with 0.5 – 25 wt% nitric acid that is used as an oxidizing agent.

(2) A method for cleaning a silicon wafer is further characterized by a cleaning liquid comprised of an aqueous solution that contains 0.05 – 10 wt% hydrogen fluoride during the silicon wafer cleaning process, along with 0.05 – 10 wt% hydrogen peroxide that is used as an oxidizing agent.

(3) A method for cleaning a silicon wafer is further characterized by a cleaning liquid comprised of an aqueous solution that contains 0.05 – 10 wt% hydrogen fluoride during the silicon wafer cleaning process, along with oxidizing gas bubbles that are mixed into the solution to be used as an oxidizing agent.

3. Detailed Description of the Invention

Industrial Field of Application

This invention pertains to a cleaning method designed to provide a high level of cleanliness along the surface of a silicon wafer.

Prior Art

In recent years, the high level of integration within devices has brought a strong demand for an improved level of cleanliness along the surface of the silicon wafers that are used as substrates for these devices.

When minute contaminants (also referred to as particles) exist along the surface of a silicon wafer, such as silicon particles, dust, etc., this can result in disconnections and shorts along the wires within a device, and in cases where metallic contaminants exist such as transition metals, other problems can arise such as the occurrence of defects along the oxidation inductive lamination layer, as well as a drop in the lifetime of the device. For this reason, when a cleaning process is conducted for the purpose of removing these contaminants, it is also necessary to prevent contamination during the cleaning process.

Recently, the following methods have been used for cleaning silicon wafers: (1) a method in which cleaning is conducted using a diluted hydrogen fluoride solution, (2) a method in which cleaning is conducted using a mixed solution of either hydrochloric acid or sulfuric acid and hydrogen peroxide, and (3) a method in which cleaning is conducted using a mixed solution of ammonia and hydrogen peroxide. The cleaning liquid

used in each of these cleaning methods contains water and a highly pure form of chemicals designed to maximize the reduction of minute particle contaminants and transition metal contaminants.

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Among the previous methods noted above, method (1) is capable of dissolving a natural oxide film with a normal thickness of 10Å on a silicon wafer surface, and while this method is highly effective at removing metallic contaminants within the oxide film, it still presents some difficulty when it comes to reducing the level of minute particle contaminants.

Method (2) is able to use a high level of dissolution capability with respect to the metallic contaminants contained within the sulfuric acid, but it is incapable of dissolving an oxide film. For this reason, it is highly effective when it comes to removing metallic contaminants located on top of an oxide film, but it has very little effect when it comes to removing metallic contaminants that are located within an oxide film or along the interface between an oxide film and silicon.

Since method (3) works to dissolve the silicon itself, it is highly effective at removing metallic contaminants located on top of the silicon layer. However, due to the fact that the oxide film that is generated within the basic cleaning solution can easily become embedded with the metallic contaminants, etc., that exist within the cleaning solution, there is a high possibility that the silicon wafer will become contaminated once again. However, due to the fact that this method is highly effective at removing minute particles, it is widely used among wafer manufacturers and device manufacturers.

In addition, as a method for resolving the problems experienced with the prior methods noted above, the so-called Slight Etch method was introduced in which a silicon wafer is cleaned by being dipped into a mixed solution of 60 wt% nitric acid and a maximum of 0.1 wt% hydrogen fluoride. (Ritsuo Takizawa, et al., "Extended Abstracts of Solid State Devices and Materials, 1988, P. 475)

However, highly pure nitric acid, which is referred to as semiconductor grade nitric acid, still contains ppb-order or sub-ppb-order metallic contaminants such as Al, Ca, Cu, Fe, K, Na, Zn, etc. Accordingly, there is a high concentration of metallic contaminants within cleaning solutions that contain a high concentration of nitric acid, such as 60 wt%. Furthermore, when a cleaning tank made of quartz glass is used, the metallic impurities within the quartz glass become eluted into the solution, causing the concentration to gradually increase.

Also, with the high oxidation strength of highly concentrated nitric acid, an oxide film forms on the surface of silicon wafers, and the metallic contaminants within the cleaning solution can easily become embedded within this oxide film. Therefore, even when the Slight Etch method is applied, there is a limit to the level of high purification that takes place with regard to the silicon wafers.

Problem to Be Solved by the Invention

A method for evaluating the purity of silicon wafer surfaces is one in which the lifetime (hereinafter referred to as the recombination lifetime) is investigated using the microwave reflection method. Using this method, the inventors have evaluated the purity of silicon wafers that were cleaned according to each type of method available. The results showed that in cases where Fe is included in the cleaning solution during cleaning operations in which a mixed solution of ammonia and hydrogen peroxide is used, contamination occurs along the silicon wafer surface at a level of approximately 8×10^{11} atoms/cm^2 even when the Fe amount is very low at 0.5 ppb. It is further understood that this causes a drop in the recombination lifetime. (Otsuka, et al., The 34th Semiconductor and Integrated Circuit Technology Symposium, Preliminary Findings, 1988, P. 37)

The objectives of this invention are as follows: to significantly reduce the level of minute particle contaminants as well as metallic contaminants such as Fe when cleaning silicon wafers; to eliminate quality problems such as the occurrence of defects along the oxidation inductive lamination layer, as well as drops in lifetime; and to obtain a highly pure silicon wafer that will prevent degradation of electrical properties when used in devices.

An outline of this invention follows.

(1) A method for cleaning a silicon wafer is characterized by a cleaning liquid comprised of an aqueous solution that contains 0.1 – 20 wt% hydrogen fluoride during the silicon wafer cleaning process, along with 0.5 – 25 wt% nitric acid that is used as an oxidizing agent.

(2) A method for cleaning a silicon wafer is further characterized by a cleaning liquid comprised of an aqueous solution that contains 0.05 – 10 wt% hydrogen fluoride during the silicon wafer cleaning process, along with 0.05 – 10 wt% hydrogen peroxide that is used as an oxidizing agent.

(3) A method for cleaning a silicon wafer is further characterized by a cleaning liquid comprised of an aqueous solution that contains 0.05 – 10 wt% hydrogen fluoride during the silicon wafer cleaning process, along with oxidizing gas bubbles that are mixed into the solution to be used as an oxidizing agent.

This invention is designed to minimize the amount of additives for the purpose of significantly reducing the level of impurities in a cleaning solution when a cleaning operation is conducted for silicon wafers. In addition, a cleaning solution with a superior level of cleaning capability is used. Specifically, this invention calls for an oxidizing agent to be added to a highly acidic aqueous solution containing a minimal amount of fluorine ions. Furthermore, as the oxide film along the silicon wafer surface is dissolved, an etching capability is provided for the silicon, making it possible to effectively remove metallic contaminants such as Fe, etc. Claim (1) notes that a minimal amount of nitric acid is used as an oxidizing agent, whereas Claim (2) notes that a minimal amount of hydrogen peroxide is used, and Claim (3) notes that an oxidizing gas is used.

According to this invention, the respective concentrations of hydrogen fluoride, nitric acid, and hydrogen peroxide within the cleaning solution are given in weight percentages of HF, HNO_3, and H_2O_2. In Claim (3), it is possible to use an oxidizing gas that contains oxygen as well as nitrous oxide (dinitrogen monoxide). Furthermore, an ultrapure form of water is used as a solvent.

In Claim (1), given less than 0.1 wt% of hydrogen fluoride and less than 0.5 wt% of nitric acid, the removal effect with regard to the metallic contaminants is insufficient. If the hydrogen fluoride concentration is increased to exceed 20 wt%, a trend is recognized in which the amount of minute particle contaminants increases along the surface of the silicon wafers. Furthermore, if the nitric acid concentration is increased to exceed 25 wt%, there is an excessive amount of etching along the silicon surface, resulting in a defective wafer surface with a cloudy appearance. Thus, if the maximum concentration of hydrogen fluoride is set to 20 wt% and the maximum concentration of nitric acid is set to 25 wt%, there is no substantial problem with regard to the concentration of impurities that become intermixed from the chemicals.

Therefore, the concentration of hydrogen fluoride has been set to a range of 0.1 – 20 wt%, and that of nitric acid has been set to a range of 0.5 – 25 wt%. Note that if the cleaning solution temperature is allowed to increase beyond the required level, this will cause the hydrogen fluoride as well as the water and nitric acid to escape in the form of steam and may result in a cleaning solution that falls outside the scope prescribed by the

invention. Furthermore, increasing the temperature requires more time, which could result in a significant loss of productivity. Therefore, the preferred maximum temperature is 80°C.

In Claim (2), given less than 0.05 wt% of hydrogen fluoride and less than 0.05 wt% of hydrogen peroxide, the removal effect with regard to the metallic contaminants is insufficient. If the hydrogen fluoride concentration is increased to exceed 10 wt%, a trend is recognized in which the amount of minute particle contaminants increases along the surface of the silicon wafers. Furthermore, if the hydrogen peroxide concentration is increased to exceed 10 wt%, there is an excessive amount of etching along the silicon surface, resulting in a defective wafer surface with a cloudy appearance. Thus, if the maximum concentration of hydrogen fluoride is set to 10 wt% and the maximum concentration of hydrogen peroxide is set to 10 wt%, there is no substantial problem with regard to the concentration of impurities that become intermixed from the chemicals.

Therefore, the concentration of hydrogen fluoride has been set to a range of 0.05 – 10 wt%, and that of hydrogen peroxide has been set to a range of 0.05 – 10 wt%. Note that if the cleaning solution temperature is allowed to increase beyond 80°C, this will cause uneven cleaning such that pits may form on the silicon wafer surface after the heat treatment is conducted. Therefore, the preferred maximum temperature is 80°C.

In Claim (3), given less than 0.05 wt% of hydrogen fluoride and no intermixing of oxidizing gas bubbles, the removal effect with regard to the metallic contaminants is insufficient. If the hydrogen fluoride concentration is increased to exceed 10 wt%, the amount of minute particle contaminants increases along the surface of the silicon wafers, and at the same time, the etching amount becomes excessive, resulting in a defective wafer surface. Thus, if the maximum concentration of hydrogen fluoride is set to 10 wt%, there is no substantial problem with regard to the concentration of impurities that become intermixed from the chemicals. Furthermore, since a highly pure form of an oxidizing gas can be relatively easily obtained which has a very low concentration of impurities, this poses no problem.

Therefore, the concentration of hydrogen fluoride has been set to a range of 0.05 – 10 wt%, and oxidizing gas bubbles are intermixed to be used as an oxidizing agent. Note that if the cleaning solution

temperature is allowed to increase beyond 80°C, this will cause uneven cleaning such that pits may form on the silicon wafer surface after the heat treatment is conducted. Therefore, the preferred maximum temperature is 80°C.

In order to intermix the oxidizing gas bubbles within the cleaning solution, it is possible to use a means that is already well-known, such as inserting a gas introduction tube into the cleaning tank or installing gas jets along the bottom of the cleaning tank such that the gas is allowed to bubble into the tank.

Based on this invention, there is an electrochemical coupling between the anodic dissolution reaction of the silicon that occurs between the silicon and fluorine ions, and the cathodic reaction that is caused by the oxidizing agent, resulting in a movement of the corrosion potential to the anode side. This makes it easy to remove the metallic contaminants from the silicon wafer surface.

Passive membranes comprised of silicon oxides are either chemically or electrochemically dissolved within the highly acidic aqueous solution containing fluorine ions that fall within the scope of the method discussed in this invention. Due to the fact that this will cause stripping of the silicon wafer surface, it is necessary to add a certain amount of oxidizing agent, and when the corrosion potential moves to the anode side, the metal contaminants are easily removed from the wafer surface.

Note that according to the method described in this invention, substances other than those noted above as components of the cleaning solution may also be added without causing a loss of cleaning capability. Examples include salt types such as ammonium fluoride, etc.

In addition, according to the method of this invention, it is also acceptable to use prior well-known forms of cleaning methods in conjunction with this method. As an example, for greater effect, cleaning can be conducted using a mixed solution of ammonia and hydrogen peroxide, followed by another cleaning in which a diluted fluorine aqueous solution is used, after which cleaning is finally conducted using the method of this invention.

Embodiments

<1> Embodiment for Claim 1

The surfaces of silicon wafers are contaminated with the following: approx. 270 x 10^{10} atoms/cm^2 of Cr, approx. 240 x 10^{10} atoms/cm^2 of Cu, approx. 2230 x 10^{10} atoms/cm^2 of Fe, and approx. 313 x 10^{10} atoms/cm^2 of Ni. These wafers are then dipped into the various cleaning solutions listed in Table 1, which provides the results for each cleaning. Immediately after cleaning, the silicon wafers are cleaned twice for at least five minutes each under ultrapure running water, after which they are spun dry and an analysis is conducted to determine the level of metallic contamination on the surface.

During the analysis, chemical etching using a concentrated fluorine and nitric acid solution is applied to dissolve a 1 μm surface layer, after which the metallic element concentration within this solution is measured using a frameless atomic absorption photometry analysis method. Note that ND indicates a level that falls below

the lower limit for analytical determination. Also note that Cr is less than 0.1 x 10^{10} atoms/cm^2, Cu and Fe are less than 0.2 x 10^{10} atoms/cm^2, and Ni is less than 2.0 x 10^{10} atoms/cm^2.

The minute particles on the wafer surface are measured using a wafer surface particulate measuring device, and those wafers showing 10 particulates per wafer or less are indicated with an O, whereas those showing more than 10 particulates per wafer are indicated with an X.

In addition, a visual judgment is made as to whether the wafer surfaces after cleaning are hydrophobic or hydrophilic. Those that are hydrophobic are indicated with an O, those that are slightly hydrophobic are marked with a , and those that are hydrophilic are marked with an X. A hydrophobic surface indicates that a silicon oxide, namely and oxide layer, does not exist on the silicon wafer surface.

An optical microscope is then used in order to observe whether or not there are any pitting defects along the wafer surface, and the findings are included in the table. The absence of pits indicates that the etching amount is appropriate, such that the wafer has an extremely smooth mirror surface.

In Table 1, Comparison Examples 1 and 15 show that the residual amounts of Fe and Cu are particularly high due to the low levels of hydrogen fluoride during cleaning. In the same fashion, Comparison Examples 6 and 14 show a high occurrence of pitting as well as residual minute particle contamination due to the fact that the hydrogen fluoride levels are too high. Pitting defects also occur in the cases of Comparison Examples 19 and 20 due to the fact that the nitric oxide levels are too high.

Prior Art Example No. 21 in which the Slight Etch cleaning method is applied uses an aqueous solution that has 60 wt% of HNO3 and 0.1 wt% of HF, but the removal effect is low with regard to Fe. Prior Art Example No. 22 in which the Ammonia Hydrogen Peroxide cleaning method is applied uses an aqueous solution that has 4.1 wt% of NH_3 and 4.4 wt% of H_2O_2, and among the various cleaning methods, this one has the lowest removal effect with regard to metallic contaminants, especially in the case of Fe. Prior Art Example No. 23 in which the Chlorine Hydrogen Peroxide cleaning method is applied uses an aqueous solution that has 5.1 wt% of HCl and 4.4 wt% of H_2O_2, and although this method is currently the most widely used due to its

metallic contaminant removal effect, it still has a low removal effect with regard to Fe when compared to the examples given for this invention.

Example (1) of this invention shows a significant reduction in both minute particle contaminants as well as metallic contaminants, with no evidence of pitting defects on the surface after cleaning. Furthermore, the surface is shown to be hydrophobic after cleaning, with no existence of an oxide film. This means that the type of recontamination that occurs when cleaning is performed in such a way that an oxide film is formed during cleaning and metallic contaminants within the cleaning solution are allowed to become embedded within the oxide film has not occurred in the case of Example 1 of this invention.

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<2> Embodiments for Claims 2 and 3

The surfaces of silicon wafers are contaminated with the following: approx. 18 x 10^{10} atoms/cm^2 of Cr, approx. 110 x 10^{10} atoms/cm^2 of Cu, approx. 110 x 10^{10} atoms/cm^2 of Fe, and approx. 21 x 10^{10} atoms/cm^2 of Ni. These wafers are then dipped into the various cleaning solutions listed in Table 2, which provides the results for each cleaning. The cleaned wafers then undergo the same procedures as noted in Embodiment <1> with regard to water rinsing and drying, followed by an analysis of the metallic contaminants, measurements regarding minute particle contaminants, and observations of pitting defects. The results are shown in Table 2.

Examples (2) and (3) of this invention, which are the respective embodiments of Claims (2) and (3) of this invention, show that the levels of metallic contaminants and minute particle contaminants are drastically reduced, with no evidence of pitting defects.

Due to the low levels of hydrogen fluoride and hydrogen peroxide used during cleaning in the case of Comparison Example No. 8, as well as the low level of hydrogen fluoride used during cleaning in the case of Comparison Example No. 9, both of these examples show high residual amounts of Cr, Cu, and Fe. In the case of Comparison Example No. 15, the low level of oxidizing agent used during cleaning results in high residual amounts of Cr, Cu, and Fe. Also, as shown in Comparison Examples No. 16, No. 17, and No. 18, excessive amounts of hydrogen fluoride and hydrogen peroxide result in the appearance of pitting defects as well as an increase in the level of minute particle contaminants.

Table 1

No.	HNO_3 (%)	HF (%)	Third Com-po-nent (NH_4F)	Clean-ing Time (sec.)	Sol. Temp. (°C)	Heavy metal contamination on Surface after cleaning (x 10^{10} atoms/cm^2)				Surface After Cleaning	Pitting Defects	Min. Part. Cont.	Class.
						Cr	Cu	Fe	Ni				
01	0.50	0.05	None	300	25	61	2.3	23	ND	X	None	O	CE
02	0.10	0.10	None	300	25	2.4	20	15	ND		None	O	CE
03	0.50	5.00	None	300	25	ND	ND	ND	ND	O	None	O	PE1
04	0.50	10.0	None	300	25	ND	ND	ND	ND	O	None	O	PE1
05	0.50	20.0	None	300	25	ND	ND	ND	ND	O	None	O	PE1
06	0.50	30.0	None	300	25	ND	ND	ND	ND	O	Yes	X	CE
07	0.50	5.00	0.1%	300	25	ND	ND	ND	ND	O	None	O	PE1
08	0.50	5.00	None	300	40	ND	ND	ND	ND	O	None	O	PE1
09	0.50	5.00	None	300	60	ND	ND	ND	ND	O	None	O	PE1
10	0.50	5.00	None	300	80	ND	ND	ND	ND	O	None	O	PE1

11	15.0	0.10	None	300	25	ND	ND	ND	ND	O	None	O	PE1
12	15.0	0.10	0.1%	300	25	ND	ND	ND	ND	O	None	O	PE1
13	15.0	20.0	None	300	25	ND	ND	ND	ND	O	None	O	PE1
14	15.0	30.0	None	300	25	ND	ND	ND	ND	O	Yes	X	CE
15	25.0	0.05	None	300	25	ND	1.8	3.3	ND	X	None	O	CE
16	25.0	0.10	None	300	25	ND	ND	ND	ND	O	None	O	PE1
17	25.0	5.00	None	300	25	ND	ND	ND	ND	O	None	O	PE1
18	25.0	10.0	None	300	25	ND	ND	ND	ND	O	None	O	PE1
19	30.0	5.00	None	300	25	ND	ND	ND	ND	O	Yes	O	CE
20	30.0	20.0	None	300	25	ND	ND	ND	ND	O	Yes	O	CE
21	Slight Etch Method			300	70	ND	2.8	34	ND	X	None	O	PAE
22	Ammonia Hydrogen Peroxide Method			600	80	2.7	2.4	77	ND	X	None	O	PAE
23	Chlorine Hydrogen Peroxide Method			600	80	ND	ND	15	ND	X	None	O	PAE

[Translator's Note: In the Classification (Class.) column above, CE = Comparison Example; PE1 = Patent Example (1); PAE = Prior Art Example]

Table 2

No.	HF (%)	H_2O_2 (%)	Oxidiz-ing Gas Com-posi-tion (%)	Third Com-po-nent	Clean-ing Time (sec.)	Sol. Temp. (°C)	Heavy metal contamination on Surface after cleaning (x 10^{10} atoms/cm^2)				Pitting Defects	Min. Part. Cont.	Class.
							Cr	Fe	Ni	Cu			
01	0.05	1.00	None	None	600	25	ND	ND	ND	ND	None	O	PE2
02	0.51	0.10	None	None	600	25	ND	ND	ND	ND	None	O	PE2
03	0.10	2.01	None	None	600	25	ND	ND	ND	ND	None	O	PE2
04	0.50	0.12	None	None	600	25	ND	ND	ND	ND	None	O	PE2
05	1.05	0.11	None	None	360	25	ND	ND	ND	ND	None	O	PE2
06	1.00	1.07	None	NH_4F 0.10%	240	25	ND	ND	ND	ND	None	O	PE2
07	0.99	5.00	None	None	120	25	ND	ND	ND	ND	None	O	PE2
08	0.03	0.04	None	None	600	25	8.2	6.8	ND	5.3	None	O	CE
09	0.01	1.00	None	None	600	25	ND	23.4	ND	12.4	None	O	CE
10	0.10	0.20	None	None	600	40	ND	ND	ND	ND	None	O	PE2
11	0.05	None	Pure O_2	None	600	25	ND	ND	ND	ND	None	O	PE3
12	0.15	None	80%O_2+ 20%Ar	None	600	25	ND	ND	ND	ND	None	O	PE3
13	1.01	None	20%O_2 +80%N_2	NH_4F 0.10%	360	30	ND	ND	ND	ND	None	O	PE3
14	0.02	None	Pure O_2	None	360	25	ND	45.8	ND	7.9	None	O	CE
15	0.15	0.01	None	None	600	25	ND	12.4	ND	8.4	None	O	CE
16	11.0	2.05	None	None	600	25	ND	ND	ND	ND	None	X	CE
17	5.95	10.2	None	None	600	25	ND	ND	ND	ND	Yes	O	CE
18	11.2	None	Pure O_2	None	600	25	ND	ND	ND	ND	Yes	X	CE
19	1.00	None	20%N_2O + 80%N_2	None	600	30	ND	ND	ND	ND	None	O	PE3

[Translator's Note: In the Classification (Class.) column above, CE = Comparison Example; PE2 = Patent Example (2); PE3 = Patent Example (3)]

Effect of the Invention

When a silicon wafer is cleaned using the method described in this invention, a highly pure silicon wafer can be obtained in which the levels of metallic contaminants and minute particle contaminants are significantly reduced. Furthermore, not only does this invention make it possible to avoid a drop in quality among silicon wafers, such as the occurrence of defects along the oxidation inductive lamination layer as well as a drop in lifetime, when these wafers are used in highly integrated devices such as IC, LSI, etc., it is also possible to prevent degradation of electrical properties in these devices.

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Reference No.
Job No. TOT-LYON-2268A

19. Japan Patent Office (JP) 11. Patent Application Laid-open No.

12. Japan Laid-open Patent Gazette (A) Showa 62-117330(1987)

51. Int. Cl.[5]	ID Code	Internal Reference No.	43. Patent Laid-open Date: May 28, 1987 (Showa 62)
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SPECIFICATION

1. Title of the invention Semiconductor Wafer Cleaning Method

2. Claims

(1) A semiconductor wafer cleaning method, characterized in that a semiconductor wafer is immersed in a cleaning liquid composed of ammonia, sulfuric acid, hydrochloric acid or other substance, whereupon ozone is supplied to the aforementioned cleaning liquid.

3. Detailed description of the invention

Field of industrial utilization

The present invention concerns a method for cleaning semiconductor wafers, and in particular, concerns a method for cleaning semiconductor wafers wherein oxygen is supplied during cleaning.

Prior art

In the past, methods for cleaning semiconductor wafers, as shown in Figure 2, have involved introducing a dilute solution containing 10% or less of such substances as sulfuric acid (H_2SO_4), aqueous ammonia (NH_4OH), hydrochloric acid (HCl) and hydrofluoric acid (HF) into a cleaning vessel 11, and heating this cleaning liquid 13 to approximately 80°C with a heater 12. The semiconductor wafer is cleaned by immersing it in this liquid 13. In order to improve the cleaning activity, hydrogen peroxide (H_2O_2) is added dropwise to the cleaning liquid 13 immediately prior to introduction of the semiconductor wafer so that oxygen is generated, thereby achieving greater cleaning uniformity.

[1] ILS Note – An alternative way of reading this person's name is Hiroshi.

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This type of method is common knowledge in, for example, Japanese Unexamined (Kokai) Patent Application No. Sho 59-46032 (H 01 L 21/304).

Problems to be solved by the invention

However, various disadvantages have resulted from the type of method described above. Firstly, there is the disadvantage that water is generated due to thermal decomposition resulting from the use of hydrogen peroxide, and the cleaning liquid 13 is thus additionally diluted, producing non-uniform cleaning which results in a loss of surface uniformity of the semiconductor wafer. For this reason, the defect density of oxide films formed by thermal oxidation increases, and the surface condition becomes non-uniform during polysilicon cleaning.

Secondly, there is the disadvantage that the cleaning liquid 13 is contaminated by contaminants contained in the liquid because hydrogen peroxide is used, so that a clean cleaning process is not carried out.

Thirdly, if the attempt is made to improve cleaning efficiency by increasing the temperature of the cleaning liquid 13, there is the disadvantage that thermal decomposition of the hydrogen peroxide will accelerate, and the cleaning effects will actually be compromised.

Means for solving the problems

The present invention was developed in light of the disadvantages described above, and offers a cleaning method for semiconductor wafers wherein past disadvantages have been dramatically mitigated by means of supplying ozone to the cleaning liquid.

Action

In accordance with the present invention, ozone gas is introduced into the cleaning liquid 4 during cleaning, so that oxygen can be supplied in constant quantities and dilution of the cleaning liquid 4 can be stopped.

Working examples

The cleaning method for semiconductor wafers pertaining to the present invention is described below in reference to Figure 1.

A 90-96% concentrated sulfuric acid stock solution (H_2SO_4), ammonia aqueous solution (NH_4OH), hydrochloric acid (HCl), nitric acid (HNO_3) or hydrofluoric acid (HF) is diluted to 10% or less and is introduced as cleaning liquid 4 into a cleaning vessel 1, where a pipe 2 composed of quartz or Teflon is installed below the cleaning vessel 1 in such a manner that ozone (O_3) is blown upwards from below. A heater 3 is installed below the cleaning vessel 1 for heating the cleaning liquid 4. With sulfuric acid, heating is performed at 100-140°C, whereas with ammonia aqueous solution, heating is performed at 80-100°C.

A semiconductor wafer that is held on a stand is immersed in this cleaning vessel 1, and ozone is introduced from the pipe 2 so that the semiconductor wafer is cleaned while supplying oxygen ions into the cleaning liquid 4.

In this method, oxygen ions are continuously supplied without accompanying dilution of the cleaning liquid 4 because ozone is a gas. By this means, oxidation of the cleaned surface is facilitated and a hydrophilic treatment is carried out, so that an extremely clean cleaning process can be performed with good reliability.

Characteristic curves used for representing cleaning effects in the cleaning method of the present invention and a conventional cleaning method are shown in Figure 3. In comparing the method of the present invention wherein $NH_4OH + O_3$ is used and a method known as a conventional RCA cleaning method wherein $NH_4OH + H_2O_2$ is used, the heating temperature has been restricted to 80-90°C in the past due to thermal decomposition of the H_2O_2, and the cleaning effects deteriorate as indicated by the arrow due to dilution of the liquid with water generated by thermal decomposition: H_2O_2 //arrow// H_2O + O*//upwards arrow//. With the present invention, however, ozone is used so that cleaning effects are greatly improved because heating can be performed at 100°C or greater. In addition, the method of the present invention that employs $H_2SO_4 + O_3$ provides effects that are similar to those of conventional methods that employ $H_2O_4 + H_2O_2$.

Effect of the invention

Firstly, the present invention has the advantage that ozone is used as the source for generating oxygen ions, so that the cleaning liquid 4 is not diluted, and cleaning is activated by the oxygen ions. As a result, cleaning can be reliably and uniformly carried out at the surface of the semiconductor wafer.

Secondly, the invention has the advantage that ozone is a gas, and thus there is no danger of pollution of the cleaning liquid 4 with contaminants when this substance is introduced, so that cleaning can be performed

without contamination.

Thirdly, the invention has the advantage that, because ozone is used, oxygen ions can be supplied in constant amounts even if the temperature of the cleaning liquid 4 is increased, because there is no connection with thermal degradation of H_2O_2. The cleaning effects can thus be increased by two or more times over past methods.

Fourthly, the invention has the advantage that, because ozone is used, H_2O_2 liquid need not be managed, which simplifies management from the standpoint of safety relative to cases where H_2O_2 is used.

Brief description of the figures

Figure 1 is a cross-sectional diagram describing the cleaning method for semiconductor wafers pertaining to the present invention, Figure 2 is a cross-sectional diagram describing a conventional method for cleaning semiconductor wafers, and Figure 3 is a graph for showing the cleaning effects obtained in the past and with the present invention.

1 Cleaning vessel
2 Pipe
3 Heater
4 Cleaning liquid

Figure 1

Figure 2

Figure 3
1 Cleaning effects (relative scale)
2 Temperature